

Thermal Desorption Study of Physical Forces at the PTFE Surface

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D.R. Wheeler and S.V. Pepper
Lewis Research Center
Cleveland, Ohio

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D.R. Wheeler and S.V. Pepper
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

SUMMARY

Thermal desorption spectroscopy (TDS) of the polytetrafluoroethylene (PTFE) surface was successfully employed to study the possible role of physical forces in the enhancement of metal-PTFE adhesion by radiation. The thermal desorption spectra were analyzed without assumptions to yield the activation energy for desorption over a range of xenon coverage from less than 0.1 monolayer to more than 100 monolayers. For multilayer coverage, the desorption is zero-order with an activation energy equal to the sublimation energy of xenon. For submonolayer coverages, the order for desorption from the unirradiated PTFE surface is 0.73 and the activation energy for desorption is between 3.32 and 3.36 kcal/mol; less than the xenon sublimation energy. The effect of irradiation is to increase the activation energy for desorption to as high as 4 kcal/mol at low coverage.

INTRODUCTION

The adhesion between polytetrafluoroethylene (PTFE) and metals is of practical importance. Good dielectric and thermal properties make PTFE useful in electronic applications where it is desirable to increase the adhesion of metal films to the PTFE. In many mechanical applications a strong bond is required between a metal substrate and a PTFE film, and in tribological applications, it is necessary that the transfer film of PTFE formed during sliding adhere well to the metal counterface. In all these cases, it would be desirable to increase the normally low adhesion between metal and PTFE.

It has been found that metal films adhere better to irradiated PTFE than to virgin PTFE, whether the radiation is ions (ref. 1), electrons (ref. 2), or x-rays (ref. 3). Understanding this improvement could help in understanding the bond between metals and unirradiated PTFE. The improved adhesion on irradiated PTFE can be due to one or more of three types of effect (ref. 4); topographic changes (e.g., mechanical interlocking), chemical interactions, or physical (dispersion) forces. Mechanical forces are unlikely in the present case, because no transfer of the PTFE to the metal is observed when the bond fails (ref. 1). Furthermore, the enhanced adhesion is observed upon irradiation with either x-rays or ions which produce substantially different topographic changes in the surface of the PTFE (ref. 3). There is some x-ray photoelectron spectroscopic (XPS) evidence for chemical interaction between nickel films and irradiated PTFE (ref. 3). However the data could not be interpreted unambiguously, and since the PTFE is damaged by the x-rays used for analysis, the technique is open to question. Physical forces are always present between materials. While much weaker per atom than chemical forces, they act over the entire contact area and can thus be an appreciable part of the total bond between macroscopic surfaces. The question is whether the physical forces are increased by irradiation and whether they can account for the increased adhesion. To date, there is no evidence on either of these points.

Inert gas adsorption is commonly used as a probe of physical interactions on surfaces. One of the usual techniques is thermal desorption spectroscopy (TDS) (ref. 5). To the best of our knowledge, it has not been used on polymer surfaces. The purpose of the present study was twofold; first, to develop the TDS technique for xenon desorption from planar polymer surfaces and second to use the technique to determine the change in physical forces at the PTFE surface upon irradiation with electrons.

EXPERIMENT

Thermal desorption experiments were performed in an ultrahigh vacuum chamber fitted as shown schematically in figure 1. The chamber was pumped with a 150 L/s turbopump and a titanium sublimation pump. A nude ion gauge, out of the line of sight of the specimen, was used to monitor the background pressure in the chamber and also to measure the pressure rise during the TDS experiments. The pressure in the chamber, before beginning a TDS experiment, was less than 8×10^{-11} torr. A cryostat regulated the sample temperature. Xenon was directed onto the specimen through a microcapillary array from a calibrated ballast volume. The chamber also incorporated an electron gun for irradiation of the sample and apparatus (not shown in figure 1.) for x-ray photoelectron spectroscopy (XPS) of the specimen surface.

A TDS experiment consisted of exposing the specimen at 30 K to a given dose of xenon. The temperature of the specimen was then increased linearly to 120 K at a rate of 0.1 K/s, and both the specimen temperature and the pressure in the chamber were recorded. Under the rapid pumping speed conditions of this experiment, the pressure rise is proportional to the desorption rate of xenon from the PTFE surface (ref. 6). The resulting curve of pressure versus temperature is the thermal desorption spectrum. The pressure, temperature pairs were digitized and stored in a microcomputer. Some details of the specimen preparation, the dosing procedure and the cryostat are presented here.

Specimen Preparation

The PTFE surfaces used for TDS were prepared by spinning a commercial dispersion of PTFE onto copper caps which could be screwed onto the cryostat used to regulate the sample temperature. Before use, the coated caps were annealed in vacuum to between 410 and 415 °C for 15 min to drive off the carrier and sinter the PTFE film. Scanning electron microscopy of the specimens showed the filamentary structure typical of specimens prepared in this way (ref. 7). They undoubtedly had a surface area greater than the geometric area.

Irradiated PTFE samples were prepared in the same way. They were then exposed to a 1 kV electron beam. The beam was rastered over the surface of the specimen. The effective current density was $2.2 \mu\text{A}/\text{cm}^2$, and the sample was irradiated for 180 min. Irradiation was performed in the vacuum system in which the TDS experiments were performed, and the sample was not exposed to air between irradiation and TDS analysis.

Samples prepared for TDS were examined with XPS before and after irradiation. Because the x-ray irradiation used to obtain the XPS spectra causes damage to the PTFE (ref. 8), samples that were used for TDS experiments were not analyzed by XPS until after the TDS experiments were complete. The XPS

spectrum of the unirradiated PTFE specimens was characteristic of clean, undamaged PTFE. No impurities could be detected, and there was no trace of copper or oxygen lines from the copper substrate. The change upon irradiation was the same as had been observed previously (ref. 8).

Doser

The apparatus used to dose the specimen with xenon consisted of a micro-capillary array connected through a bakable valve to an ion pumped ballast volume. Pressure in the ballast volume was monitored with an ion gauge. The amount of xenon to which the specimen was exposed was calculated from the drop in pressure in the known ballast volume during dosing. From the area of the specimen exposed to xenon and the diameter of the xenon atom, the number of monolayers which would result from a particular amount of xenon on a geometrically smooth surface was calculated. In the data to follow, that number of monolayers is referred to as the dose.

The actual coverage of xenon on the PTFE after dosing depended on the true surface area of the specimen and the sticking coefficient of the xenon as well as on the dose. It has already been noted that the true surface area was greater than the apparent area. Furthermore, during dosing, there was a slight pressure rise in the main chamber which indicated that the sticking coefficient was less than one. However, the pressure rise and the time it lasted were both more than an order of magnitude less than the pressure increase and time of a TDS. Thus, the sticking coefficient must be greater than 0.99. In any case, the actual xenon coverage was proportional to the area under a TDS curve. In all the data below, the coverage of xenon is calculated from the area under the TDS spectrum. The unit is torr-sec. As a point of reference, the coverage produced by a xenon dose of one monolayer was 6.1×10^{-7} torr-sec. That coverage is indicated as 1 mL in the data below.

In principle, the thickness of the xenon layer on the PTFE could be measured by the attenuation of the XPS lines from the PTFE or by angle resolved XPS. Both methods were tried, but it was found that the radiation used for XPS was sufficient to cause progressive damage to the PTFE during the analysis. This produced variable xenon adsorption. Furthermore, the radiation damaged PTFE was not stable during the rather long times required for XPS analysis. Finally, the inelastic mean free path of low energy electrons in xenon, which is required for the analysis, is not well known. As a result, the true monolayer coverage of xenon could not be found precisely. It was found that a dose of 1 mL produced a coverage of between 0.2 and 0.5 mL as determined by XPS.

Cryostat

The sample was mounted on a continuous flow liquid He refrigerator. The refrigerator incorporated a heater for temperature control and a thermocouple for temperature measurement. Because the thermocouple was separated from the sample surface, the actual sample temperature could differ by several tenths of a degree from the indicated temperature. Furthermore, the discrepancy varied throughout a day of operation. The temperature of the peak in the TDS from a standard dose of xenon was used to correct for this temperature drift.

Thus, temperatures reported here are consistent to within 0.2 K, but the absolute temperature error could be as large as 0.5 K.

It was found that readsorption of the xenon from the specimen onto other cold areas of the cryostat produced serious artifacts in the TDS. This was a particular problem at the low ramp rate of 0.1 K/sec used here. Readsorption was controlled by adding a room temperature shield to the cryostat as shown in figure 1. Clearance between the shield and the cold specimen is minimal, and the amount of desorbed xenon reaching other parts of the cryostat is not detectable in the spectrum. Furthermore, to assure that the cryostat and specimen are cleared of xenon, the specimen temperature is raised to 220 K between runs.

RESULTS

Thermal desorption spectra were obtained for a wide range of xenon doses on virgin and irradiated PTFE. We will consider the general features of the spectra first and then turn to an analysis of the thermodynamic relationship between the pressure, temperature and xenon coverage represented by each point on a spectrum.

General Features

The TDS curves fell naturally into two families; those for multilayer initial coverage and those for submonolayer initial coverage. Each family will be considered separately.

Multilayer coverage. The general shape of the TDS for initial coverage greater than 1.3×10^{-4} torr-sec (about 21 mL) is illustrated by the spectrum of figure 2(a). There was a characteristic rapid decrease in pressure at high temperature. Figure 2(b) shows the low temperature (high coverage) region of two such spectra. The pressures and therefore the desorption rates in this temperature range were the same for a wide range of coverage. The variation in temperature of the TDS peak maximum is shown in figure 3. In the region of multilayer coverage, the peak temperature increased with the coverage. All of these observations are consistent with zero-order desorption kinetics (ref. 9). In addition, figure 3 shows that the TDS peak temperature was independent of substrate irradiation, in the multilayer coverage region.

Low coverage. Spectra obtained at submonolayer coverages are shown in figures 4(a) and (b). They did not exhibit shapes characteristic of any simple desorption model. In particular, they did not appear to be produced by first-order desorption. This is confirmed by the variation of the temperature of the peak maximum shown in figure 3. At submonolayer coverage, the peak temperature decreased with increasing coverage. In the case of simple, first-order desorption, the temperature of the peak would remain constant. The varying peak temperature could be attributed either to a distribution of binding energy sites on the surface or to fractional order desorption produced by lateral interactions between xenon atoms (ref. 9).

Comparison of the high temperature sides of the two peaks in figure 4(a) suggests that irradiation produced some increase in the number of high energy binding sites. The effect of radiation on the substrate is even more apparent

in figure 4(b). The TDS peak on the irradiated specimen was almost 10 K higher than the peak on the unirradiated specimen. The effect of radiation on the substrate is also evident in the submonolayer coverage region of figure 3. Below 2×10^{-7} torr-sec, the maximum pressure always occurred at higher temperatures for the irradiated PTFE than for the unirradiated PTFE.

Thermodynamic Analysis

Because we wish to determine the strength of the xenon-PTFE interaction, we are particularly interested in the low coverage data. Had the desorption been first-order, a simple Redhead analysis would yield the desorption energy (ref. 6). However, in the present case we resort to analysis based explicitly on the Arrhenius equation (ref. 5):

$$r = \nu C^n \exp(-E/RT), \quad (1)$$

where r is the desorption rate, ν is the "frequency factor," C the coverage, n the order of desorption, E the activation energy for desorption, R the gas constant and T the temperature. Most analyses of TDS assume that ν is independent of coverage, and further, that it has a value of 10^{13} s^{-1} . We do not make these assumptions but proceed as follows.

The pressure at each point in a TDS is proportional to the desorption rate of xenon from the surface. This rate depends on both the temperature and the coverage at that temperature. The temperature can be determined directly. The coverage is proportional to the integral under the TDS curve from the temperature of interest to the highest temperature. On each TDS, temperature, pressure and coverage values were obtained at half degree intervals up to the peak of the curve. The pressure and coverage at one temperature were measured on TDS curves for a variety of initial doses. These were combined to produce a plot of pressure versus coverage at that temperature.

A typical plot for virgin PTFE is shown in figure 5. The logarithmic coverage scale allows presentation of a wide range of coverage but has no other significance. At very low coverage, the desorption rate must, of course, approach zero. As the coverage increases, so does the desorption rate, but the increase is not linear as it would be for first-order desorption. At a coverage of 9×10^{-6} torr-sec (15 mL), the desorption rate drops and then remains constant for higher coverage. Coverage independent desorption rate is the signature of zero-order desorption kinetics.

Curves of pressure versus coverage were constructed every half-degree for temperatures between 50 and 60 K. Below 50 K, the pressure rise was not large enough to be measured reliably, while there were too few data points above 60 K. Reading the pressure at a particular coverage from each curve in this series yields the pressure as a function of temperature for that coverage. An Arrhenius plot of the natural log of the pressure versus the inverse of the temperature can then be made. Figure 6 is a typical Arrhenius plot. The linearity of these plots is confirmation that equation (1) holds with a single energy in the range of temperature and coverage analyzed. The slope of the best line through the data is $-E/R$.

Arrhenius plots were constructed for a range of coverages, and the desorption energies determined. The result is shown in figure 7. For reference,

the sublimation of xenon is also shown (ref. 10). As can be seen, the desorption energy at high coverage was in reasonable agreement with the sublimation energy. As the coverage decreased, the desorption energy decreased until it reached a value of 3.34 ± 0.03 kcal/mol below 1 monolayer coverage.

The same analysis was performed on the TDS from the irradiated PTFE surface. Because the surface was not stable, fewer TDS curves could be acquired. However, some desorption energies could be extracted in the coverage range from 10^{-7} to 10^{-5} torr-sec. These are also shown in figure 7. It can be seen that the energies were the same as those for virgin PTFE above 1 monolayer. At low coverage, however, the desorption energy from irradiated PTFE was larger than that from virgin PTFE and exceeded even the sublimation energy of xenon.

A plot of the intercepts of the Arrhenius plots versus the natural-log of the coverage is shown in figure 8. According to equation (1), the slope of this line is the order n of desorption which is 0.73 in this case. The linearity of the plot confirms that the order and the preexponential, ν , are constants. There were insufficient data for a similar analysis on the irradiated surface.

DISCUSSION

To the best of our knowledge, this is the first report of the application of thermal desorption spectroscopy to a polymer surface. Therefore, the first part of the discussion will address the experimental technique, itself. Next, conclusions will be drawn on the nature of the adsorption of xenon on the virgin PTFE surface. Finally, the effect of irradiation of PTFE on xenon adsorption and its significance for adhesion will be discussed.

Experimental Technique

The experiment reported here differs in ramp speed from most reported flash desorption experiments (refs. 5, 6, and 9). The low ramp speed was required to assure temperature uniformity in the cryostat used. The uniformity is demonstrated by the sharpness of the TDS curves. The sharp drop on the high temperature side of the multilayer peak in figure 2(a) demonstrates the response of which the system is capable. It also shows that the specimen temperature was uniform.

Because the ramp speed in this experiment was so low, the possibility of readsorption on the sample during the ramp must be considered (ref. 5). In fact, it was found that the Arrhenius plots displayed a slight departure from linearity at pressures above 5×10^{-8} torr. This was attributed to effects of readsorption at high desorption rate, and pressures above this value were, therefore, excluded from the analysis. The linearity of the Arrhenius plots is one evidence for the validity of the data. The fact that the desorption energy at high coverage was nearly equal to the sublimation energy of xenon is additional evidence.

The nondestructive nature and surface sensitivity of the TDS give it unique capabilities for the analysis of surfaces such as that of PTFE. It was found that the TDS spectrum was sensitive to radiation-produced changes in the

surface that could not be detected by XPS. Indeed, the unstable nature of the irradiated surface was only evident from the variability of the xenon desorption spectra.

Adsorption/Desorption on Virgin PTFE

For multilayer coverage, the TDS curves are characterized by peak-temperatures that increase with coverage, identical low temperature behavior for all coverages and sharp high temperature edges. These are all features of zero-order desorption. This is confirmed by plots of pressure versus coverage which show that the pressure (and hence the desorption rate) were independent of coverage above 15 monolayers. Zero-order desorption kinetics can be produced by a variety of processes,¹¹ the most obvious being sublimation from bulk xenon. In the present case, the agreement between the desorption energy at high coverage and the sublimation energy of xenon confirms the obvious interpretation.

For submonolayer coverage, the energy of desorption was less than the sublimation energy of xenon. Clearly, the xenon-PTFE interaction energy was less than the xenon-xenon interaction energy. The low energy of interaction with the substrate and the fractional order of the desorption make it likely that lateral interactions were affecting the desorption energy.^{9,11} It seems likely that xenon islands were present on the PTFE surface. In that case, the desorption energy can only be an upper limit to the single-atom, xenon-PTFE interaction energy.

The plot of pressure versus coverage in figure 5 clearly shows an abrupt change in desorption rate in the intermediate range of coverage between one and several monolayers. Without further evidence, it is not possible to interpret this transition in detail, but it is certainly related to the change from desorption influenced by the substrate to sublimation of bulk xenon.

Effect of Irradiation

At coverage less than 1 monolayer, the desorption energy of xenon from irradiated PTFE was 3.85 to 4.0 kcal/mol, whereas it was only 3.32 to 3.36 kcal/mol from virgin PTFE in the same coverage range. Furthermore, the TDS peaks were 10 K higher for the irradiated substrate. It seems clear that the interaction between xenon and irradiated PTFE was stronger than between xenon and virgin PTFE. It is unlikely that chemical bonding was involved between xenon and PTFE, so the increased interaction is attributed to increased dispersion forces.

What changes can irradiation produce in PTFE that would enhance these dispersion forces? The changes in the C(1s) XPS spectrum of irradiated PTFE were previously interpreted as evidence for crosslinking in the surface region of the polymer.⁸ The density of the surface region could be increased by crosslinking. The increased density would, in turn, lead to increased dispersion forces.¹² However, the instability of the irradiated PTFE surface when probed by TDS suggests that the change is not entirely structural. Irradiation is known to produce trapped, long-lived radicals in PTFE.¹³ It seems probable that the optical polarizability of these radicals would be different

from that of PTFE. The presence of radicals then could well affect the dielectric properties and hence the dispersion forces at the PTFE surface.

Whatever the cause of the increased dispersion forces, they can certainly contribute to the adhesion of thin metallic films to PTFE. Since there also seem to be chemical differences in the effect of irradiation on the adhesion of different metals,² any explanation of the effect of radiation on adhesion must take into account both chemical and physical forces.

CONCLUSION

Thermal desorption spectroscopy of xenon from irradiated and virgin PTFE has been successfully performed. Analysis of the TDS curves and the desorption kinetics in the 50 to 60 K range showed the following

1. Desorption from multilayers of Xe on either surface proceeded by zero-order kinetics with an activation energy equal to the Xe sublimation energy.
2. At a coverage below 3 to 7 true monolayers the desorption behavior changed abruptly from the multilayer case and was different on irradiated and unirradiated PTFE substrates.
3. For submonolayer coverages on irradiated PTFE the activation energy was 3.85 to 4.0 kcal/mole, which was the highest observed.
4. For submonolayer coverages on unirradiated PTFE the desorption energy was 3.34 ± 0.03 kcal/mole (less than the sublimation energy of Xe), and the desorption was fractional order, indicating significant lateral interactions.

It can be concluded that the Xe-Xe interaction was stronger than the Xe-PTFE interaction on unirradiated PTFE. Irradiating PTFE increased the dispersion forces between Xe and PTFE.

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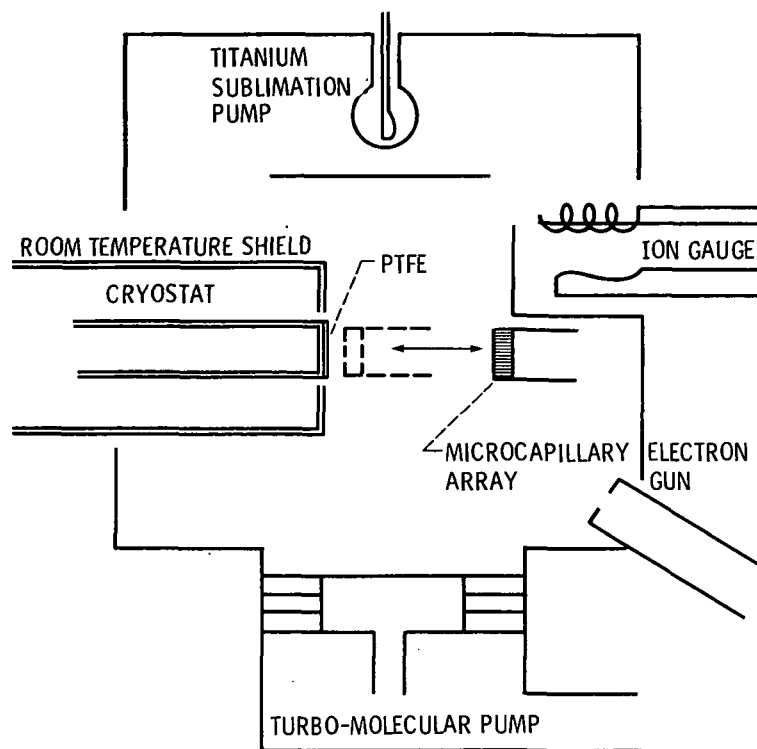
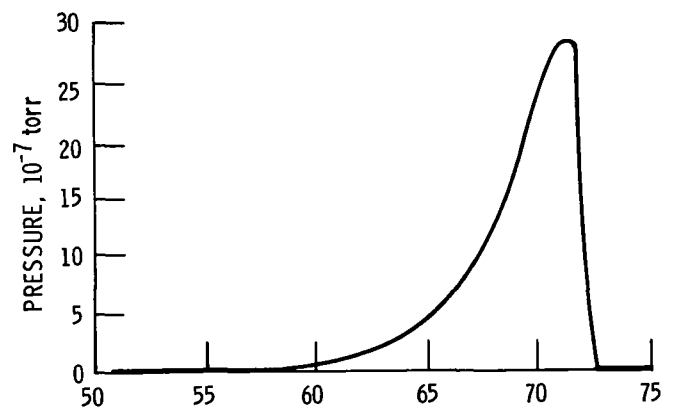
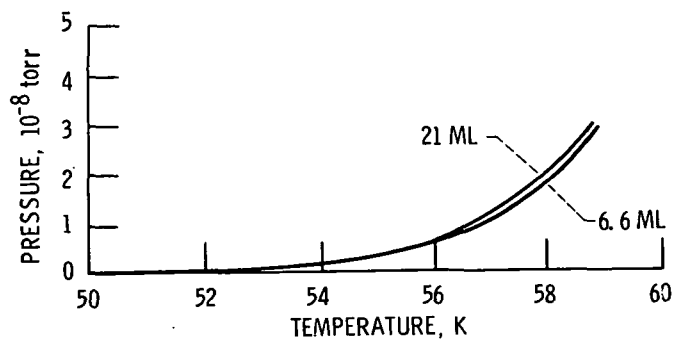


Figure 1. - Schematic representation of the thermal desorption spectroscopy apparatus.



(a) Initial coverage of 1.3×10^{-4} torr-sec (21 monolayers).



(b) Initial coverages of 4×10^{-5} and 1.3×10^{-4} torr-sec (6.5 and 21 monolayers, respectively).

Figure 2. - Thermal desorption spectra of xenon on PTFE.

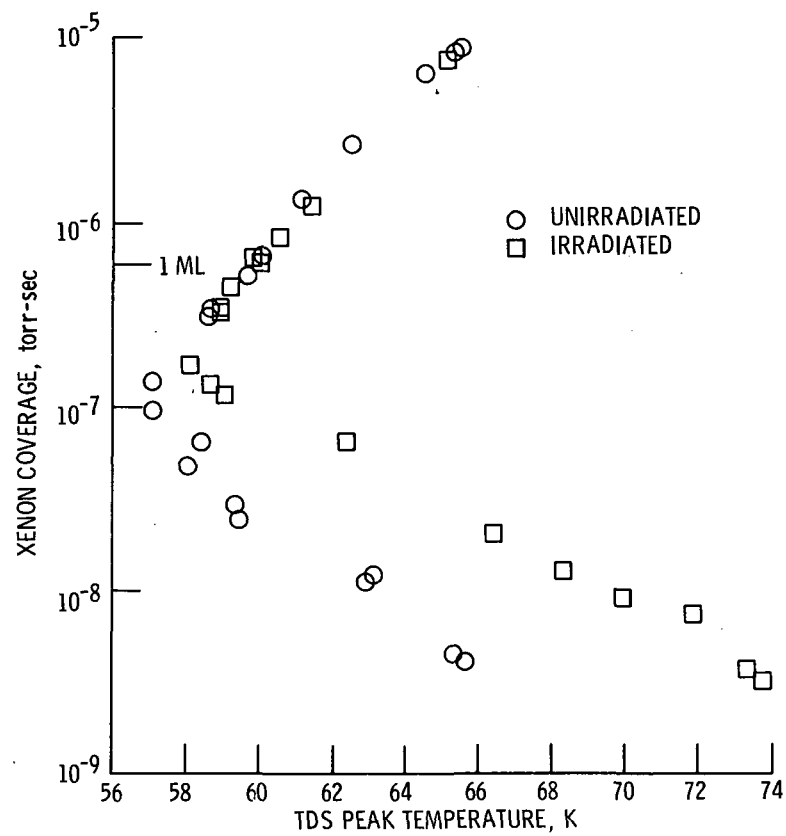


Figure 3. - Dependence of TDS peak maximum on initial coverage.

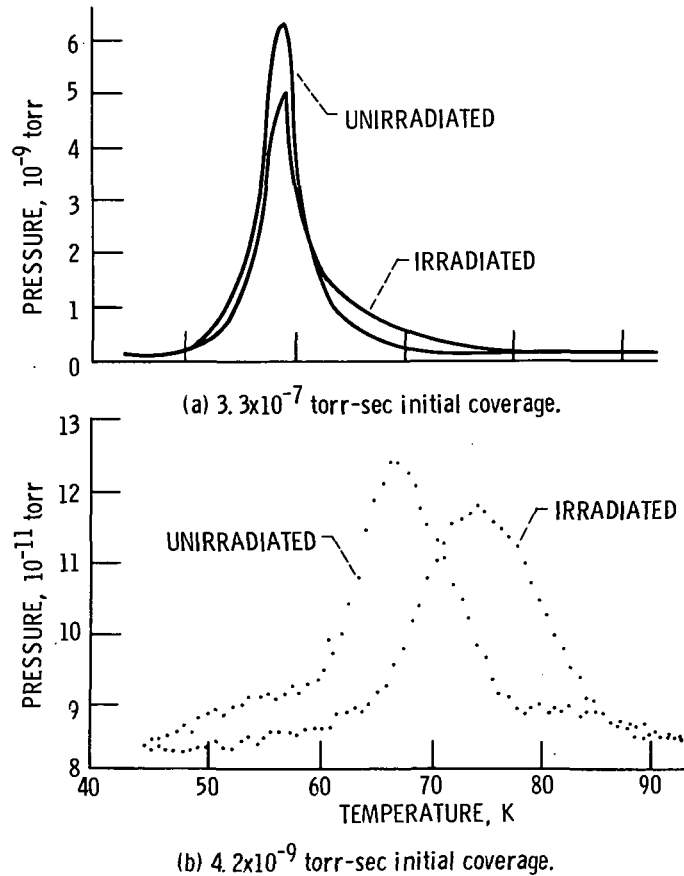


Figure 4. - Thermal desorption spectra for irradiated and unirradiated PTFE substrates.

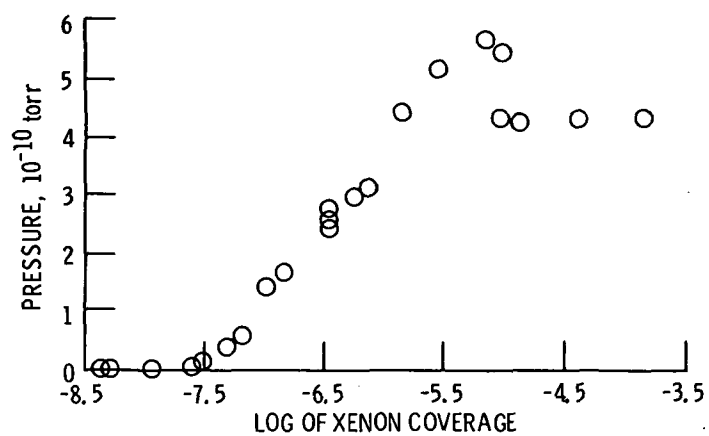


Figure 5. - Xenon pressure as a function of coverage at 52 K, unirradiated PTFE surface.

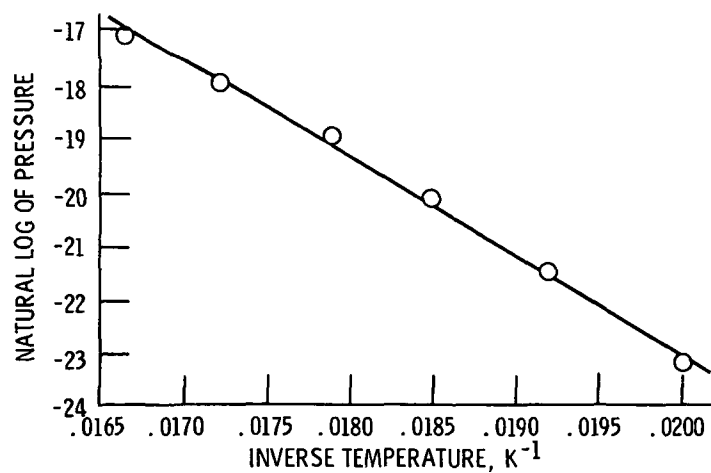


Figure 6. - Arrhenius plot: Natural log of the pressure vs inverse temperature for xenon coverage of 1×10^{-5} torr-sec on unirradiated PTFE.

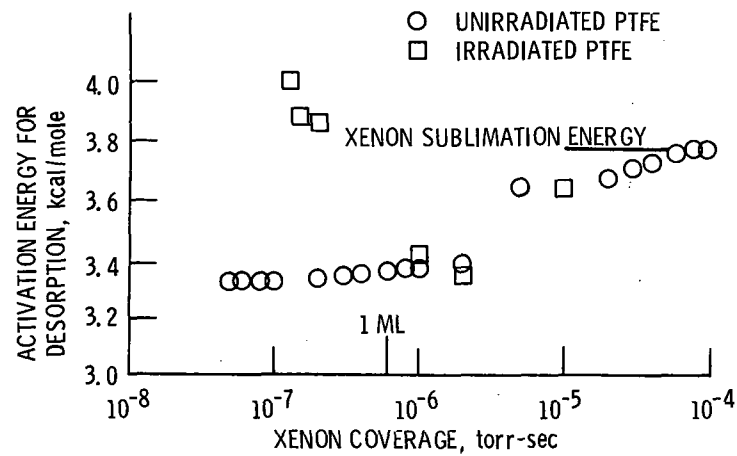


Figure 7. - Activation energy for desorption as a function of xenon coverage in the temperature range of 50 K to 60 K.

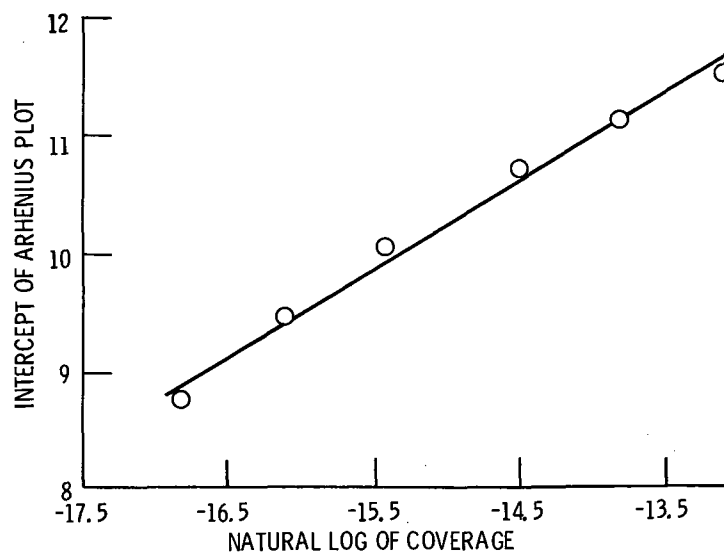


Figure 8. - Intercept of arrhenius plots vs natural log of the xenon coverage unirradiated PTFE.

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